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2,938,933

SYNTHESIS OF AROMATIC HYDROCARBONS

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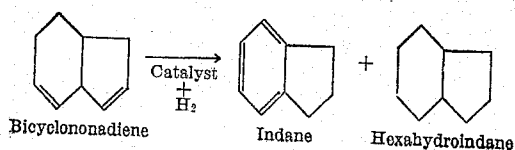
10 Claims. (Cl. 260—668)

This invention relates to the production of aromatic dicyclic hydrocarbons from nonaromatic dicyclic hydrocarbons. More particularly, the invention relates to the production of indane from a dicyclic nonadiene using mild reaction conditions.

Aromatic hydrocarbons are in considerable demand due to their many uses to the chemical manufacturing industry in producing solvents, organic acids, synthetic fibers, paints, plastics, and other chemicals. Some of these aromatic compounds are present in petroleum fractions and are produced in considerable quantities by modern refining techniques. However, in many cases, petroleum aromatic hydrocarbons are very difficult and expensive to separate. This is particularly true when specific aromatic hydrocarbons, such as indane, are present in small or trace quantities. However, the dicyclic olefinic hydrocarbons are more easily separated. In the aromatization of naphthenes or cyclic olefins temperatures in the range of 800°–1,000° F. and pressures of 200–400 p.s.i.g. are normally required. I have discovered a method which requires about atmospheric pressure and no more than 500° F. to produce in good yield aromatic dicyclic hydrocarbons from their corresponding nonaromatic dicyclic hydrocarbons. These aromatic hydrocarbons can be readily oxidized to products such as phthalic anhydride which has many uses in the paint and plastics industry.

One object of this invention is to provide a process for producing aromatic dicyclic hydrocarbons from dicyclic olefinic hydrocarbons. Another object of this invention is to provide a process for introducing a nonaromatic dicyclic nonyl hydrocarbon to a reaction zone to catalytically convert the nonyl hydrocarbon to a dicyclic hydrocarbon having a saturated ring and an aromatic ring, specifically indane.

In practicing my invention a nonaromatic dicyclic olefinic hydrocarbon containing at least one six-membered ring, such as bicyclodecene, bicyclodecadiene, bicyclononene, bicyclononadiene, or alkyl substituted homologs thereof, is charged at substantially atmospheric temperature and pressure along with hydrogen to the top of the reaction zone containing a hydrogenation catalyst. The reactor is maintained under adiabatic conditions (autogenous pressures and maximum temperature of 500° F.) and the aromatized product is withdrawn from the bottom and separated from the other products and the unreacted hydrogen. Thus, by simple distillation a dicyclic aromatic compound is obtained which can be oxidized to produce phthalic anhydride which is useful as an intermediate for paint and plastics. This reaction is exemplified as follows:



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It is highly unexpected that under such mild conditions the unsaturated bonds will shift so as to completely hydrogenate the five-membered ring while simultaneously dehydrogenating the six-membered ring to produce an aromatic. It would normally be expected that the dicyclic nonadiene would be saturated either to the dicyclic nonene or to the completely saturated hexahydroindane. While it might be expected that the five-membered ring could be saturated there is no reason to believe that the product would be dehydrogenated so as to produce three unsaturated bonds in the six-membered ring, thus producing an aromatic compound, whereas the charge contained only two unsaturated bonds. Heretofore, in order to produce aromatic compounds from their corresponding nonaromatic compounds, it has been necessary to operate above 800° F. and at superatmospheric pressures. By the practice of my invention, one can produce dicyclic aromatics in good yield by simply charging dicyclic olefins or diolefins at atmospheric pressure and temperature to a reaction zone maintained at about atmospheric pressure and adiabatic conditions. The temperature is controlled at a slightly elevated temperature of about 250° to 500° F. by regulating the flow of the reactants through the reaction zone. The heat to the reaction zone is supplied only by the exothermic heat of reaction. The pressures in the reactor at these temperatures are no higher than about 50 to 100 pounds per square inch gage. Lower pressures, which give good yields and conversions, are normally used. Preferably, pressures from atmospheric to 50 p.s.i.g. are desirable.

The following examples are illustrative of my invention, through it should be understood that it may be illustrated by other examples and is not intended to be restricted in any way by this particular description. The charge was a bicyclononadiene hydrocarbon obtained from a high boiling distillate fraction produced in the pyrolysis of low molecular weight paraffins, such as ethane and propane or mixtures thereof. The high boiling distillate fraction is produced as a condensation product which is separated, using an absorption oil, from the cracked products of the cracking operation. The production of such unsaturated distillates containing bicyclononadiene is described and claimed in F. J. Smith U.S. Patent 2,535,606, issued December 26, 1950. The unsaturated oil contains about 22% of the bicyclononadiene fraction which can be separated by simple distillation.

In the practice of my invention the bicyclononadiene fraction obtained from the above cracking operation was charged to the top of the reaction zone containing nickel on kieselguhr as a hydrogenation catalyst. The bicyclononadiene was introduced as a liquid at atmospheric temperature and pressure and permitted to pass downflow through the reactor along with about 100 cu. ft. of hydrogen per barrel of olefin at a weight hourly space velocity of about 2 to 13 ($W_o/W_c/hr.$), preferably 4 to 8 ($W_o/W_c/hr.$). The temperature rises due to the exothermic heat of reaction. The temperature which is in the order of 250° to 500° F. and preferably 350° to 450° F. is maintained at adiabatic conditions. The reaction product contains a mixture of indane, hexahydroindane, and in some cases, depending upon the space velocity used, unconverted bicyclononadiene. These compounds can be separated by distillation.

The hydrogenation catalyst used in the examples was 1/8-inch pelleted nickel on kieselguhr. However, nickel on other supports and any of the highly active hydrogenation-dehydrogenation catalysts can be used, such as platinum on alumina, copper chromite, palladium on charcoal, etc.

The effect of space velocity and temperature on the yield of indane is shown in Table 1.

Table 1

Space Velocity, W _o /W _c /hr.	Max. Temp., ° F.	Pressure, p.s.i.g.	Vol. Per- cent Indane	Vol. Per- cent Hexahy- droindane	Vol. Per- cent Un- converted Bicyclo- nonadiene
2-----	318	0	20	80	0
6-----	434	0	55	45	0
13.5-----	462	0	30	30	40

As can be seen, at an hourly weight space velocity of 6 W_o/W_c/hr., the maximum temperature of the adiabatic reaction zone was 434° F. Under these conditions, the indane content of the product was 55 vol. percent and the hexahydroindane produced was 45 vol. percent. When the space velocity was reduced to 2, a temperature of only 318° F. was obtained and the indane content of the product was 20 vol. percent, and the hexahydroindane produced was 80 vol. percent. But when the space velocity was increased to 13.5 W_o/W_c/hr. the temperature varied from 430° to 462° F., and an incomplete reaction was obtained. Analysis of the product showed that 30% indane, 30% hexahydroindane, and 40% bicyclononadiene was recovered. Therefore, the space velocity can be controlled at about 6 W_o/W_c/hr. in order to produce the maximum amount of the dicyclic aromatic compound, indane. Thus, it is shown that the amount of indane produced is a function of space velocity under adiabatic conditions. Thus, as the space velocity is increased from 2 W_o/W_c/hr. the dehydrogenation is increased and concurrently the hydrogenation decreases. However, at between 6 to 13.5 space velocity the distribution of the hexahydroindane and indane levels off at about 1:1 ratio with the unconverted bicyclononadiene increasing as the space velocity increased. Therefore, the preferred space velocity is from 4 to 8 W_o/W_c/hr.

Other dicyclic olefinic hydrocarbons are converted to aromatic compounds by use of the above method. Bicyclodecene or bicyclodecadiene is converted to tetralin when charged to my process. Likewise, bicyclononene is converted to indane.

What I claim is:

1. The process of synthesizing aromatic hydrocarbons which comprises introducing a nonaromatic dicyclic olefinic hydrocarbon containing at least one six-membered ring together with hydrogen into a reaction zone containing a hydrogenation-dehydrogenation catalyst, maintaining said reaction zone under adiabatic conditions of

autogenous pressures and maximum temperature of 500° F., controlling the weight hourly space velocity between 2 and 13 W_o/W_c/hr., and withdrawing an aromatic-containing product.

2. The process of claim 1 wherein the reaction temperature of the adiabatic reaction zone is maintained between about 250° and 500° F.

3. The process of claim 1 wherein the weight hourly space velocity of the reactants is controlled between about 4 to 8.

4. The process of claim 1 wherein the said catalyst is nickel on kieselguhr.

5. The process of synthesizing aromatic hydrocarbons which comprises introducing liquid bicyclononadiene and hydrogen into a reaction zone containing a hydrogenation-dehydrogenation catalyst, maintaining said reaction zone under substantially adiabatic conditions of autogenous pressures and maximum temperature of 500° F., controlling the weight hourly space velocity between 2 and 13 W_o/W_c/hr., and withdrawing product from said reaction zone containing indane and hexahydroindane.

6. The process of claim 5 wherein the reaction temperature of the adiabatic reaction zone is maintained between about 250° and 500° F.

7. The process of claim 5 wherein the weight hourly space velocity of the reactants is controlled between about 4 to 8.

8. The process of claim 5 wherein the catalyst is nickel on kieselguhr.

9. The process of synthesizing aromatic hydrocarbons which comprises introducing at substantially atmospheric pressure and temperature bicyclononadiene and hydrogen into a reaction zone containing nickel on kieselguhr, said reaction zone being maintained under adiabatic conditions of autogenous pressure and at a temperature of about 350° to 450° F. by controlling the weight hourly space velocity between 4 and 8 W_o/W_c/hr., withdrawing from the said reaction zone a product containing indane and hexahydroindane and recovering by distillation the substantially pure indane.

10. The process of claim 1 wherein the dicyclic olefinic hydrocarbon is a dicyclic nonyl hydrocarbon.

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